The importance of the electronic contribution to linear magnetoelectricity

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We demonstrate that the electronic contribution to the linear magnetoelectric response, usually omitted in first-principles studies, can be comparable in magnitude to that mediated by lattice distortions, even for materials in which responses are strong. Using a self-consistent Zeeman response to an applied magnetic field for noncollinear electron spins, we show how electric polarization emerges in linear magnetoelectrics through both electronic- and lattice-mediated components – in analogy with the high- and low-frequency dielectric response to an electric field. The approach we use is conceptually and computationally simple, and can be applied to study both linear and non-linear responses to magnetic fields.

Linear magnetoelectrics are materials which respond with a change in electric polarization to a magnetic field, or conversely with a change in magnetization to an electric field: $P_i = \alpha_{ij} H_j$; $M_j = \alpha_{ij} E_i$, where α is the linear magnetoelectric tensor.

The research challenges in identifying materials with useful linear magnetoelectric (ME) responses are threefold: (i) Symmetry requirements that both space-inversion and time-reversal symmetries be broken are satisfied by few materials, (ii) materials satisfying these criteria tend to do so only in phases that develop at relatively low temperatures, and (iii) most of the MEs discovered to date have weak responses. Recently, a number of developments have led to a significant revival of activity in the search for novel magnetoelectric materials, including the observation that multiferroics can have strong ME responses[1], and the identification of the microscopic couplings that are responsible for strong and weak ME responses[2–6].

First-principles methods are emerging[6, 7] as a valuable tool for computing the strength of α in real materials without any empirical input. The methods are becoming sufficiently reliable to be used in a predictive capacity in searching for new ME materials. While many approaches have been explored or can be envisaged for computing α, ranging from a self-consistently applied electric or magnetic field, to quantum-mechanical perturbation theory in the applied field, by far the most successful and widely used approach for applications to date has been a linear-response approach based on the lattice-dynamical quantities[6–8]. However, this approach computes only the so-called "lattice-mediated" part of α and ignores purely electronic contributions to the response. The common justification is that such contributions are expected to be weak, just as in strong dielectrics the electronic response is negligible compared to the ionic contribution. In this Letter, we demonstrate, using an alternative numerical approach involving a self-consistently applied magnetic field, that the purely electronic magnetoelectric response can in fact be large, even in materials with relatively strong α in which one might expect the response to be dominated by lattice mechanisms. In fact, the electronic and ionic contributions can be of similar magnitude and opposite sign, which can lead to a weak total response while lattice-only methods would predict it to be large.

We begin by defining the different contributions to α. We define a "clamped-ion" contribution that accounts for magnetoelectric effects occuring in an applied field with all ionic degrees of freedom remaining frozen. This purely electronic contribution, α^{el}, is the response that would be measured for high-frequency fields, in analogy with the static-high-frequency dielectric response in insulators, ϵ_∞. The remaining part of the response, which emerges at low frequency so that the ions (and in principle the lattice parameters[9]) respond to the field, we label α^{latt}. α^{latt} is the difference between the total response and the electronic, so that $\alpha^{\mathrm{tot}} = \alpha^{\mathrm{el}} + \alpha^{\mathrm{latt}}$, and it is the part of the response that is accessible from linear-response theory using lattice-dynamical quantities[7]. (Note that α^{latt} also includes some electronic response through the dynamical charges).

Evaluating α^{el} requires a full quantum-mechanical treatment of the response, either using perturbation theory or a self-consistently-applied finite field. In this work, we use an applied magnetic field to compute α. Due to difficulties with periodic boundary conditions when using a full vector potential in the electronic Hamiltonian, we restrict our field to act only on the electron spin as a self-consistent Zeeman field. This means that we omit contributions to α that are derived from the orbital magnetic response[10], which are expected to be significantly weaker than the spin-derived response for most systems.

Computational Approach: Calculations of ME responses require a treatment of noncollinear spin orders. Within the Kohn-Sham framework, noncollinearity is handled by generalizing the orbitals to be complex spinors, resulting in a 2×2 spin-density matrix $(n_{\sigma\sigma'})$

that allows the magnetization density to vary in both magnitude and direction throughout the system.

In order to apply a magnetic field, we begin by making a Legendre transform of the noncollinear-spin Hohenberg-Kohn energy functional:

$$\Lambda\left[n_{\sigma\sigma'}\left(\vec{r}\right);\vec{H}\right] = E_{\mathrm{HK}}\left[n_{\sigma\sigma'}\left(\vec{r}\right)\right] - \mu_0\vec{H}.\vec{\mu}_{\mathrm{tot}}, \qquad (1)$$

where E_{HK} is the usual zero-field energy functional (consisting of non-interacting kinetic energy, external electrostatic energy, Hartree and exchange-correlation terms, and the Madelung energy of ion-ion interactions). $\vec{H}$ is the auxiliary magnetic field applied to spin degrees of freedom and $\vec{\mu}_{\mathrm{tot}}$ is the total spin magnetic moment of the system (including the Landé g factor). The spatially varying magnetic moment, $\vec{\mu}\left(\vec{r}\right)$, can be found from the four components of $n_{\sigma\sigma'}$, and $\vec{\mu}_{\mathrm{tot}}$ is its spatial integral. Subsequently, we variationally minimize Λ with respect to single-particle Kohn-Sham spinor orbitals, subject to the usual constraints on orthonormality and conservation of total particle number. The result is a term in the Kohn-Sham potential, acting on the spinor orbitals, that imposes the external magnetic field on the noncollinear spin density. Practically, this term simply shifts the relative external potential for each of the four spin manifolds:

$$\Delta V_{\sigma\sigma'} = -\frac{g}{2}\mu_B\mu_0\begin{pmatrix} H_z & H_x+iH_y \\ H_x-iH_y & -H_z \end{pmatrix}, \qquad (2)$$

which is trivially compatible with periodic boundary conditions, and which clearly reduces to the collinear case, with the field providing a different Fermi level for "up" and "down" spin channels, if $\vec{H} = (0, 0, H_z)$.

We implement Eq. 2 into the Vienna Abinitio Simulation Package (VASP)[11]. We employ a plane-wave basis set for expanding the electronic wave functions and density, and PAW potentials[12] are used for core-valence separation. We note that it is important to disable symmetrization of the wave functions in the Brillouin zone since application of a magnetic field leads to an electronic structure that breaks the crystal symmetry. We self-consistently include spin-orbit coupling in all of our calculations. This is required to obtain a magnetoelectric response for those materials in which the spin-lattice coupling derives from relativistic effects such as the antisymmetric $(\vec{s}_i \times \vec{s}_j)$ Dzyaloshinskiĭ-Moriya interaction. All of our calculations simulate a single magnetic domain, which corresponds to experiments in which a poling procedure has been performed. Since different antiferromagnetic domains contribute to α with different signs, measurements otherwise tend to provide a lower bound on the single-domain response.

Transverse magnetoelectric response of Cr_2O_3: Cr_2O_3, the first ME material to be discovered, remains the best-studied and prototypical linear magnetoelectric. Cr_2O_3 adopts the space group R$\bar{3}$c in the ground state, with Cr and O occupying Wyckoff positions 4c and 6e in the rhombohedral setting. We work with the experimental volume (95.9Å^3) and rhombohedral angle ($55.13°$)[13], but fully optimize the ion coordinates to the LDA+U ground-state (Cr: $x = 0.1536$; O: $x = 0.9426$). For the exchange-correlation potential, we use the Dudarev form of LSDA+U with $U_{\mathrm{eff}} = 2.0\,\mathrm{eV}$[7]. In the ground-state G-type antiferromagnetic (AFM) ordering, the free energy of the system contains two symmetry allowed linear magnetoelectric couplings and is of the form[14]

$$F = -\alpha_\perp\left(E_xH_x + E_yH_y\right) - \alpha_\parallel E_zH_z. \qquad (3)$$

We note that the response parallel to the trigonal (easy) axis, $\alpha_\parallel$, has been experimentally demonstrated to be close to zero at zero temperature[15]. This small low-temperature response is expected: In the absence of quantum fluctuations and orbital contributions, the low-temperature ME response should tend to zero because the spin-only parallel *magnetic susceptibility* vanishes at $T = 0\,\mathrm{K}$. Our calculations, which are formally at zero temperature and do not include quantum spin fluctuations or the orbital magnetic response, do give $\alpha_\parallel = 0$ as expected. The temperature dependence of $\alpha_\parallel$ has recently been explained using an alternative first-principles scheme[16].

For the transverse response of Cr_2O_3, $\alpha_\perp$, we first compute the electronic ME contribution with clamped ions. Upon application of a Zeeman field perpendicular to the collinear spin axis, the Cr spins cant so that the unit cell acquires a net magnetization. Our calculated spin-only magnetic susceptibility is $\chi_\perp^M = 1.9 \times 10^{-3}$ in dimensionless SI units, which compares favorably to the experimental value[17] of 1.7×10^{-3} at $78\,\mathrm{K}$. With the new spin configuration generated by the applied magnetic field, spin-orbit coupling leads to an electric polarization. Note at this stage that the lattice has not been permitted to relax in response to the field. We compute the electric polarization using the Berry phase approach[18]. The results are shown as open squares in Fig. 1, with our calculated $\alpha_\perp^{\mathrm{el}} = 0.34\,\mathrm{ps.m}^{-1}$.

The canting of spins in the applied magnetic field also causes spin-orbit-driven forces on ions. The induced forces are very small, mirroring the observed weakness of the linear ME effect in Cr_2O_3, so high numerical quality must be achieved in studying the structural distortion. We carefully converge our ionic forces with respect to basis-set size ($E_{\mathrm{cut}} = 700\,\mathrm{eV}$), k-point sampling ($6 \times 6 \times 6$), and self-consistent field iteration. We then choose a small tolerance to which forces are eliminated ($< 5\,\mu\mathrm{eV}\ \text{Å}^{-1}$).

Once the structural distortions are found for a given magnetic-field strength, we quickly estimate the ionic polarization by multiplying the ion displacements by the full Born-effective-charge tensor (see open circles of Fig. 1). This procedure leads to the lattice-mediated ME response, $\alpha_\perp^{\mathrm{latt}} = 1.11\,\mathrm{ps.m}^{-1}$. We also computed
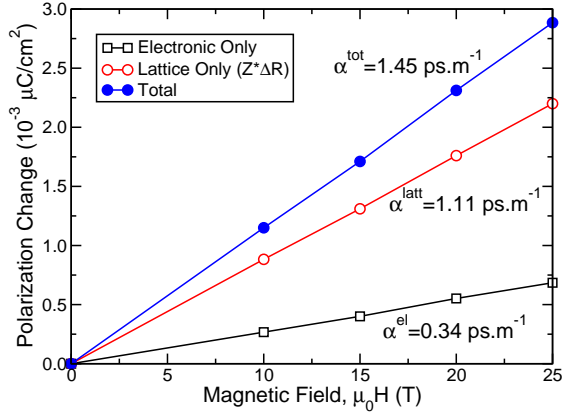
FIG. 1. (Color online) The separate contributions to the transverse magnetoelectric response of Cr_2O_3 calculated using Eq. 2. The clamped-ion response, α^{el}, is shown as open squares, and contributes approximately one fourth of the total response (filled circles). The remainder of the response is due to structural distortions in the applied field (open circles), computed using the Born effective charge tensor.

the same quantity using our parameters with the lattice-dynamical method for α^{latt} introduced previously[7] and find $0.9\,ps.m^{-1}$, in reasonably good agreement with the applied magnetic field approach.

With the lattice distortion included for each magnetic-field strength, we now fully recompute the electric polarization using the Berry-phase approach *with the magnetic field applied.* This procedure yields the full spin-mediated α, both electronic and lattice contributions, and is shown as filled circles in Fig. 1. We find $\alpha_\perp = 1.45\,ps.m^{-1}$ ($= 4.3 \times 10^{-4}\,emu$-CGS), in excellent agreement with summing $\alpha_\perp^{el}$ and $\alpha_\perp^{latt}$ as expected. From this analysis, it is clear that the electronic response, α^{el}, contributes one fourth of the total spin-driven magnetoelectric response of Cr_2O_3. The total response that we compute is in good agreement with zero-temperature extrapolations of experimental measurements, which range[7, 19, 20] from 2—$4.7 \times 10^{-4}\,emu$-CGS.

Off-diagonal ME response of LiNiPO$_4$: The lithium orthophosphates $LiMPO_4$ (M=transition metals) are currently attracting much interest because of their potential use as cathodes for Li-ion batteries, as well as for their large magnetoelectric responses and the recent observation of ferrotoroidic domains in $LiCoPO_4$[21].

Here we focus on $LiNiPO_4$ as a test case for the size of the electronic ME response. $LiNiPO_4$ has space group Pnma with 28 atoms in the primitive unit cell and four Ni^{2+} magnetic sites. We again use the experimental[22] lattice parameters for our calculations ($a = 10.032\,\text{Å}$, $b = 5.854\,\text{Å}$, $c = 4.677\,\text{Å}$) while the ionic coordinates are fully relaxed to the LDA+U ground state.

We first address the zero-field magnetic structure. Experimentally[23], the magnetic structure has been

characterized as C-type AFM with spins oriented predominantly along the c axis, combined with a weak spin canting of A-type AFM order along the a axis. The reported zero-field canting angle, θ, in the Ni compound is $7.8°$.

With a plane-wave cutoff of $500\,eV$ and $4\times4\times2$ k-point sampling, we qualitatively reproduce the observed magnetic structure in our calculations. However, the precise canting angle is strongly sensitive to the *intra*-atomic J parameter used in the Liechtenstein LDA+U procedure. For $U = 5\,eV$, a common value for Ni^{2+}, the canting angle θ varies from $1.6°$ to $7.6°$ as J is modified from 0.0 to $1.7\,eV$. Hence, a relatively large J appears to be important for quantitative agreement with the magnitude of the reported spin canting. The observed sensitivity arises from the double-counting term in the LSDA+U potential, in which the off-diagonal elements (acting on the non-collinear part of the spin density matrix) are determined by J alone. The canting angle is quite insensitive to our other simulation parameters, including the on-site Coulomb interaction, U.
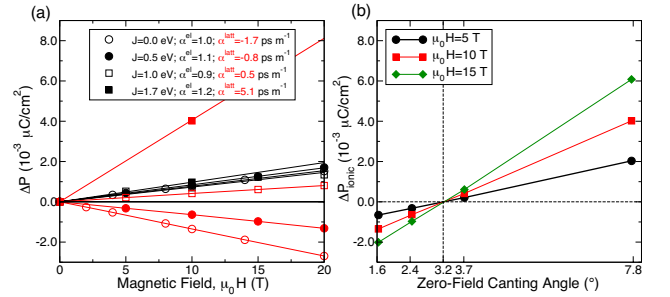

FIG. 2. (Color online) $LiNiPO_4$ data under magnetic field $\vec{H} \parallel a$: (a) Clamped-ion (black) and ionic (red) contributions to the polarization versus the magnetic field for different values of the intra-atomic Hund's coupling J. (b) Ionic polarization versus canting angle for three values of the magnetic field.

We now turn to the magnetoelectric response of $LiNiPO_4$. For the magnetic point group $mm'm$, the magnetoelectric tensor admits only two non-zero components: α_{xz} and α_{zx}. We focus on the larger component α_{zx}, which we access by computing the Berry-phase polarization along c while applying a magnetic field along the a axis ($\vec{H}$ perpendicular to the easy axis). In Fig. 2a we report both the clamped-ion and lattice-mediated magnetoelectric response under this orientation of magnetic field. For each of the four different values of the intra-atomic J, we find $\alpha_{zx}^{el} \sim 1.0\,ps.m^{-1}$. However, as might be expected from the J dependence of the spin canting angle, the ionic contributions to α is strongly sensitive to J. For $J = 0.0\,eV$, α_{zx}^{latt} is moderately large and negative. With increasing J, this component of the response progressively increases, eventually turning positive. The connection between the J dependence of α^{latt} and the
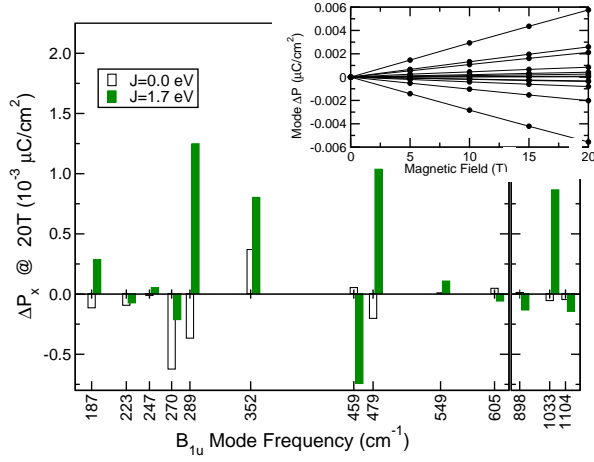
FIG. 3. (Color online) Mode contributions to the ionic polarization of LiNiPO$_4$ for a field strength of 20 T. Inset: linear evolution of each of the 13 B_{1u} (polar) lattice modes with applied field.

canting angle is highlighted in Fig. 2b, where the ionic contribution to the polarization at different values of the magnetic field strength are plotted against different initial canting angles (obtained by varying J). We observe a linear relationship between the magnetic-field induced ionic polarization and the zero-field canting angle. Interestingly, for a critical canting angle ($\theta_c \sim 3.2°$), the ionic contribution to the polarization is zero for all field strengths. Under these conditions, α_{zx}^{tot} is dominated by the electronic contribution, while for other values of the canting angle the electronic and ionic components are comparable in magnitude.

To characterize the microscopic origin of the ionic contribution to α_{zx}^{latt} in LiNiPO$_4$, we report in Fig. 3 the phonon mode decomposition of the magnetic-field induced lattice polarization for different values of J. For LiNiPO$_4$, thirteen polar (B_{1u} symmetry) modes enter in determining α^{latt}. As expected, each mode increases in strength linearly with the field (inset of Fig. 3), demonstrating that the lattice remains harmonic. Plotting the contribution to the polarization for each mode for an applied magnetic field of 20 T (Fig. 3), we find that all modes are important, so that the response is surprisingly not dominated by the softest lattice modes. The zero α^{latt} at θ_c clearly arises from an accidental cancellation between the positive and negative magnetoelectric responses of the 13 individual polar lattice modes.

Conclusion: We have demonstrated a new approach for calculating the linear magnetoelectric response of materials from first principles. The approach, which provides an efficient way to extract α even for systems with low symmetry, involves self-consistent application of a magnetic field which acts on the spin degrees of freedom only in the Zeeman sense. Orbital magnetic contribu-

tions to responses are neglected within this approach, but both electronic and ionic contributions to magnetic-field induced electric polarization are present.

We have demonstrated that the electronic contribution to magnetoelectric responses is not negligible, and can in fact dominate the total response, in contrast with prior expectations. Furthermore, we have shown for the case of LiNiPO$_4$ that the magnetoelectric response is not dominated by the softest polar lattice modes, and that a partial cancellation of the contributions from different modes occurs, weakening the magnetoelectric response of this material. These features suggest that the best route to engineering strong magnetoelectrics may not lie with strain engineering to induce lattice destabilization, but rather with strengthening the spin-lattice coupling, for example using strong non-relativistic mechanisms[6].

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